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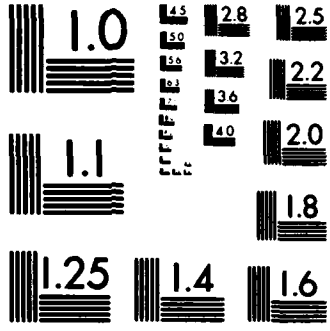

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END OF FISCAL YEAR REPORT

OCTOBER 1, 1983 - SEPTEMBER 30, 1984

N00014-82-K-0050

CHARACTERIZATION OF NOVEL BINDERS BASED ON ENERGETIC THERMOPLASTIC ELASTOMERS

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Unlimited
4. PERFORMING ORGANIZATION REPORT NUMBER(S): N00014-82-K-0050-1984A	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: L. H. Sperling, Lehigh University; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State and ZIP Code): Coxe Laboratory, #32, Bethlehem, PA 18015	7b. ADDRESS (City, State and ZIP Code)
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: Office of Naval Research; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-82-K-0050
8c. ADDRESS (City, State and ZIP Code): Dr. Richard S. Miller, 800 North Quincy Street, Arlington, VA 22217	10. SOURCE OF FUNDING NOS. — PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT NO.
11. TITLE (Include Security Classification): Characterization of Novel Binders Based on Energetic Thermoplastic Elastomers	
12. PERSONAL AUTHOR(S): Sperling, L. H.	
13a. TYPE OF REPORT: End of Fiscal Year; 13b. TIME COVERED: FROM 10/1/83 TO 9/30/84	14. DATE OF REPORT (Yr., Mo., Day): 10-26-84; 15. PAGE COUNT: 5
16. SUPPLEMENTARY NOTATION	
17. COSATI CODES — FIELD / GROUP / SUB. GR.	18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Binders, LOVA, Energetic Thermoplastic Elastomers, PolyBEMO, Block copolymers, polyethers

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Beginning in the fall of 1981, a research program was undertaken to develop a series of block copolymers based on novel polyethers. This research is part of the Low Vulnerability Ammunition, LOVA, program of the Office of Naval Research. The principal polymers of interest in this program are the crystalline polyBEMO and polyBAMO, and their thermoplastic elastomers. The most important findings of the past year are:

1. PolyBEMO decomposes endothermally at elevated temperatures, meeting an important LOVA objective of safer compositions;

2. The use temperatures of polyBEMO, polyBAMO, and their block copolymers range from -30 to +75°C;

3. The modulus of the block copolymers is leathery to rubbery, depending on the composition.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ OTIC USERS ☐	21. ABSTRACT SECURITY CLASSIFICATION
22a. NAME OF RESPONSIBLE INDIVIDUAL: Dr. Richard S. Miller	22b. TELEPHONE NUMBER (Include Area Code): (202) 696-4403; 22c. OFFICE SYMBOL

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4. Processing can be carried out in the range of 80-110°C.

5. PolyBEMO and polyBAMO are highly crystalline materials. PolyBEMO exhibits more than one crystalline form.

The major focus of the research has been to characterize the thermal and physical behavior of these materials. While the work is still incomplete, major accomplishments of the past year are as follows:

1. Thermal degradation studies on poly[3,3-bis(ethoxy methyl) oxetane], polyBEMO. This research utilized both differential scanning calorimetry, DSC, and mass spectrometry, showing that C-O bonds in both the backbone and side chains were the main source of degradation during heating. This reaction was demonstrated to be endothermic in nature, important in preventing detonation of the propellent by hot spall.

2. In a basic characterization study of di- and triblock copolymers based on polyBEMO, the melting temperature, T_m, of polyBEMO was found to be 85°C, while its glass transition temperature was found to be about -30°C. In a triblock copolymer with a random copolymer center block of poly(BNMO-co-THF), the modulus was found to be in the leathery range through the proposed application temperatures. Crystallization was found to be complete after 2-5 minutes. In terms of processing temperature range and general physical properties, these materials were found to be outstanding candidates for LOVA binder materials.

3. In the most recent study, the nature of crystallinity in polyBEMO and poly[3,3-bis(azidomethyl) oxetane], polyBAMO was examined. PolyBEMO was found to be the more crystalline, while the heat of crystallization is larger for polyBAMO. Two crystalline forms were identified by x-ray studies for polyBEMO, while only one crystalline form was found for polyBEMO. The thermodynamics of fusion were investigated via DSC and melting point depression studies, providing important energy requirements for future manufacturing needs.

Recently, much interest has been expressed on the development of thermoplastic elastomers with crystalline hard blocks, rather than glassy blocks. The main advantages of such materials include the possibility of having the two blocks being miscible in the melt, with the hard block crystallizing out on cooling. Such a system would have lower melt viscosities than corresponding products exhibiting phase separation in the melt. The present systems are giving good evidence that this may be true in important materials of LOVA interest. We think that the block copolymers based on polyBEMO, polyBAMO, and related material offer much promise in the development of novel elastomers, adhesives, and binders. As already mentioned, these materials also have melting temperatures and other properties that are known to be satisfactory.

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LIST OF PRESENTATIONS:

1. "Polyether Block Copolymers for the LOVA Program", ONR Workshop, U. Mass., MA, May 1983.

2. "Thermodynamics of Phase Separation in Crystalline Block Copolymers Based on Polyethers", Capri, Italy, International Symposium of Phase Relationships and Properties of Multicomponent Polymer Systems", May 1983.

3. "Characterization of Block Copolymers Based on PolyBEMO", ONR Workshop, Chesapeake Bay Meeting, July, 1983.

4. "Characterization of Novel Polyethers for the LOVA Program", ONR Workshop, Chestertown, MD, August, 1982.

5. "Viscoelastic Behavior of Block Copolymers Based on Polyethers", AIChE Meeting, Los Angeles, CA, November, 1982.

LIST OF PAPERS AND PUBLICATIONS:

1. R. B. Jones, C. J. Murphy, L. H. Sperling, M. Farber, S. P. Harris, and G.E. Manser, "Thermal Decomposition Behavior of Poly[3,3-bis(ethoxymethyl) oxetane] and Related Polyethers", accepted, Journal of Applied Polymer Science.

2. K. E. Hardenstine, C. J. Murphy, R. B. Jones, and G. E. Manser, "Characterization of Block Copolymers Based on Poly[3,3-bis(ethoxymethyl) oxetane] and other Novel Polyethers", accepted, Journal of Applied Polymer Science.

3. K. E. Hardenstine, G. V. Henderson, Jr., L. H. Sperling, C. J. Murphy, and G. E. Manser, "Crystallization Behavior of Poly[3,3-bis(ethoxymethyl) oxetane] and Poly[3,3-bis(azidomethyl oxetane], submitted, J. Polymer Science, Polymer Physics Edition.

L. H. Sperling

Sources of Support Fiscal Year 1984
(in addition to ONR 533613)

	Agency		Annual Support $
1.	NSF	DMR-8405053 "Structure and Morphology of IPN's Using Small-Angle Neutron Scattering and Phase Diagram Methods"	$66,000
2.	NSF	CPE-8206720 "Neutron Scattering from Latex Particles"	$66,000
3.	U.S. Navy	N00014-84-K-0508 "The Fundamental Nature of the Damping Phenomenon as Characterized with Tailored IPN Compositions"	$80,000

Personnel

Dr. L. H. Sperling, Principal Investigator

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Ms. K. E. Hardenstine, M.S. Candidate, graduated October, 1984.

Mr. R. B. Jones, M.S. Candidate, graduated June, 1984.

Mr. G. V. Henderson, M.S. Candidate

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